Thin Sol-Gel-Derived Silica Coatings on Dental Pure Titanium Casting

Keiichi Yoshida,[1] Kohji Kamada,[1] Koichi Sato,[1] Ruriko Hatada,[2] Koumei Baba,[2] Mitsuru Atsuta[1]

[1] Department of Fixed Prosthodontics, Nagasaki University School of Dentistry, Nagasaki, Japan

[2] Materials Section, Technology Center of Nagasaki, Omura, Japan

Abstract: The sol-gel dipping process, in which liquid silicon alkoxide is transformed into a solid silicon-oxygen network, can produce a thin film coating of silica (SiO_2). The features of this method are high homogeneity and purity of the thin SiO_2 film and a low sinter temperature, which are important in the preparation of coating films that can protect metallic ion release from the metal substrate and prevent attachment of dental plaque. We evaluated the surface properties of dental pure titanium casting coated with a thin SiO_2 or SiO_2/F-hybrid film by the sol-gel dipping process. The metal specimens were pretreated by dipping in isopropylalcohol solution containing 10 wt% 3-aminopropyl trimethoxysilane and treated by dipping in the silica precursor solution for 5 min, withdrawal at a speed of 2 mm/min, air-drying for 20 min at room temperature, heating at 120 °C for 20 min, and then storing at room temperature. Both SiO_2 and SiO_2/F films bonded strongly (above 55 MPa) to pure titanium substrate by a tensile test. SiO_2- and SiO_2/F-coated specimens immersed in 1 wt% of lactic acid solution for two weeks showed significantly less release of titanium ions (30.5 ppb/cm^2 and 9.5 ppb/cm^2, respectively) from the substrate than noncoated specimens (235.2 ppb/cm^2). Hydrophobilization of SiO_2- and SiO_2/F-coated surfaces resulted in significant increases of contact angle of water (81.6° and 105.7°, respectively) compared with noncoated metal specimens (62.1°). The formation of both thin SiO_2 and SiO_2/F-hybrid films by the sol-gel dipping process on the surface of dental pure titanium casting may be useful clinically in enhancing the bond strength of dental resin cements to titanium, preventing titanium ions release from the substrate, and reducing the accumulation of dental plaque attaching to intraoral dental restorations. © 1999 John Wiley & Sons, Inc. J Biomed Mater Res (Appl Biomater) 48: 778–785, 1999

Keywords: pure titanium; sol-gel dipping; silica coatings; contact angle; ion release

INTRODUCTION

Titanium is a material of choice for dental prosthetic devices such as crowns and bridges, dental implants, and removable denture frameworks,[1–5] because it is light and shows excellent corrosion resistance and biocompatibility in the oral environment compared with other dental alloys.[6,7] Further, progress in titanium casting techniques as well in shaping technologies such as CAD/CAM, will increase the future use of titanium as a restorative material.

The sol-gel dipping process,[8–13] in which liquid silicon alkoxide is transformed into a solid silicon-oxygen network, can produce a thin film coating of silica. The features of this method are high homogeneity and purity of the thin silica film and a low sinter temperature on the metal substrate, which are important for the preparation of a coating film that can be easily produced in the laboratory. This method may prevent release of metallic ions from the substrate as well as attachment by dental plaque, because the surface is smoother and more hydrophobic than noncoated metal. Resin cements are composed of various types of fillers and multi-functional methacrylate monomers, and silica is contained as a filler.[14] Silica coating on dental casting alloy surfaces using an expensive apparatus and primed treatment by silane coupling agent improved the bond strength of resin cements to silica-coated dental alloys.[15] However, since titanium is a relatively new restorative material, the effects of sol-gel-derived silica-coatings by dipping method in order to achieve a high bond strength between resin cements and dental pure titanium casting have not yet been determined in the dental field.

There have been no previous reports concerning thin film formation on the surface of dental pure titanium casting by the sol-gel dipping process to improve surface properties of

dental pure titanium. We investigated the adhesive strength between silica film and substrate, contact angle, and titanium ion release from silica-coated pure titanium in comparison with noncoated metal.

MATERIALS AND METHODS

Specimens of Pure Titanium Casting

The metal used in this study was dental pure titanium (Selec, Selec Co., Ltd., Osaka, Japan, Ti: 99.485%, O: 0.20%, Fe: 0.25%, N: 0.05%, H: 0.015%). Plates 20-mm × 10-mm × 1-mm thick were cast into an zirconia-magnesia investment (Selevest CB, Selec Co., Ltd.) with a centrifugal casting machine (Ticast Super R, Selec Co., Ltd.) and then ground sequentially through 200-, 600-, and 800-grit silicon carbide papers. The plates were then ultrasonically cleaned in isopropylalcohol and rinsed sequentially in acetone and deionized water to remove fatty debris and dust from the metal surface. This metal was used as the substrate.

Thin Silica Film Coating (SiO₂) by Sol-Gel Dipping Process

The metal specimens were pretreated in isopropylalcohol solution containing 10 wt% 3-aminopropyl trimethoxysilane (Chisso Corp., Tokyo, Japan) to promote adhesion to the silica. They were dipped for 5 min, withdrawn from the solution at a speed of 2 mm/min, and then air-dried for 20 min at room temperature. Subsequently, they were heated at 120 °C for 20 min and stored at room temperature. The silica precursor solution was prepared by mixing an alcohol solution containing tetramethoxysilane oligomer (Mitsubishi Chemical Corp., Tokyo, Japan) adjusted to pH 4.5 by methylalcohol solution containing 10 wt% p-toluenesulfonic acid (Kishida Chemical Co., Ltd., Osaka, Japan). The pretreated metal specimens were dipped in the silica precursor solution for 5 min, withdrawn at a speed of 2 mm/min, air-dried for 20 min at room temperature, heated at 120 °C for 20 min, and then stored at room temperature. This procedure of SiO₂ film coatings, as mentioned above, was replicated ten times to determine the film thickness of SiO₂ on the surface of dental pure titanium using a scanning electron microscope (Hitachi, Tokyo, Japan). The average thickness of SiO₂ films for all specimens was approximately 0.5 μm.

SiO₂/F-Hybrid Film Coating

Further metal specimens were treated by fluoride polymer solution containing 7 wt% perfluoroalkane (Asahi Glass Co., Ltd., Tokyo, Japan) after coating by SiO₂. They were dipped for 5 min, withdrawn from the solution at a speed of 2 mm/min, air-dried for 20 min at room temperature, heated at 150 °C for 60 min, and then stored at room temperature. The thickness of SiO₂/F-hybrid film was approximately 0.6 μm.

Elemental Surface Analysis

The elemental compositions of the chemical states for SiO₂- and SiO₂/F-coated specimens were analyzed by electron spectroscopy for chemical analysis (ESCA, ESCA 1000, Shimadzu Co., Ltd., Kyoto, Japan) with Mg K$_\alpha$ radiation (1253.6 eV) with a source of 8.0 kV and 30 mA under a pressure of 2×10^{-6} Pa evacuated with a turbo-molecular pump. The coated specimen was subjected to argon ion etching at 2.0 kV and 20 mA for a total etching time of 9 min under a pressure of 5×10^{-4} Pa in the spectrometer. The etching rate was 0.1 nm/s under these etching conditions. The ESCA measurements and argon ion etching were performed intermittently for determination of the changes in both amount and chemical state of the elements with depth. Quantitative analysis of the surface was carried out by computer in the ESCA spectrometer.

Adhesive Bond Strength of SiO₂ or SiO₂/F-Hybrid Film to Titanium

The adhesive bond strength of the thin SiO₂ or SiO₂/F-hybrid film to the metal substrate was measured by a tensile test. A commercial rivet-shaped aluminum stud-pin (JEOL Datum Ltd., Tokyo, Japan, disk 1 mm thick and 2.7 mm in diameter, pedicle 12 mm long and 1.6 mm in diameter, and epoxy resin adhesive attaching to disk head) was fixed onto the SiO₂- and SiO₂/F-coated metal specimens by a clip. After heating the specimens in an oven at 130 °C for 1 h and cooling to room temperature, the adhesive strength was measured using a tensile test machine (Sebastian V, Quad Group Inc., Washington D.C.) at a loading rate of 4.5 kg/s. The surfaces of debonded metal specimens were observed using scanning electron microscopy and energy-dispersive spectroscopy of X-rays (EDX) with an acceleration voltage of 20 KeV. Five replications were carried out for each specimen group.

Titanium Ion Release

10 mL of 1 wt% lactic acid (Wako Pure Chemicals Co., Ltd., Osaka, Japan) solution was put in a polyethylene bottle. One specimen for each surface condition was immersed in the bottle. Bottles were placed on an incupet-shaker (IPS-310, Iuchi Co., Ltd., Tokyo, Japan) at 37 °C for 2 weeks at one stroke a second. The concentration of titanium ions released from the metal specimens was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, SPS-1500VR, Seiko Instruments Co., Ltd., Tokyo, Japan). The quantities of titanium ions release from the metal specimens (ppb) was expressed as the amounts of titanium ions into the solution (10 mL) per unit surface area of the specimen (cm²). Three replications were carried out for each specimen group.

Contact Angle Measurement

A Type CA-D (Kyowa Interface Science Co., Ltd., Tokyo, Japan) contact angle analyzer was used to measure the contact angles of distilled water. A fixed droplet of water was
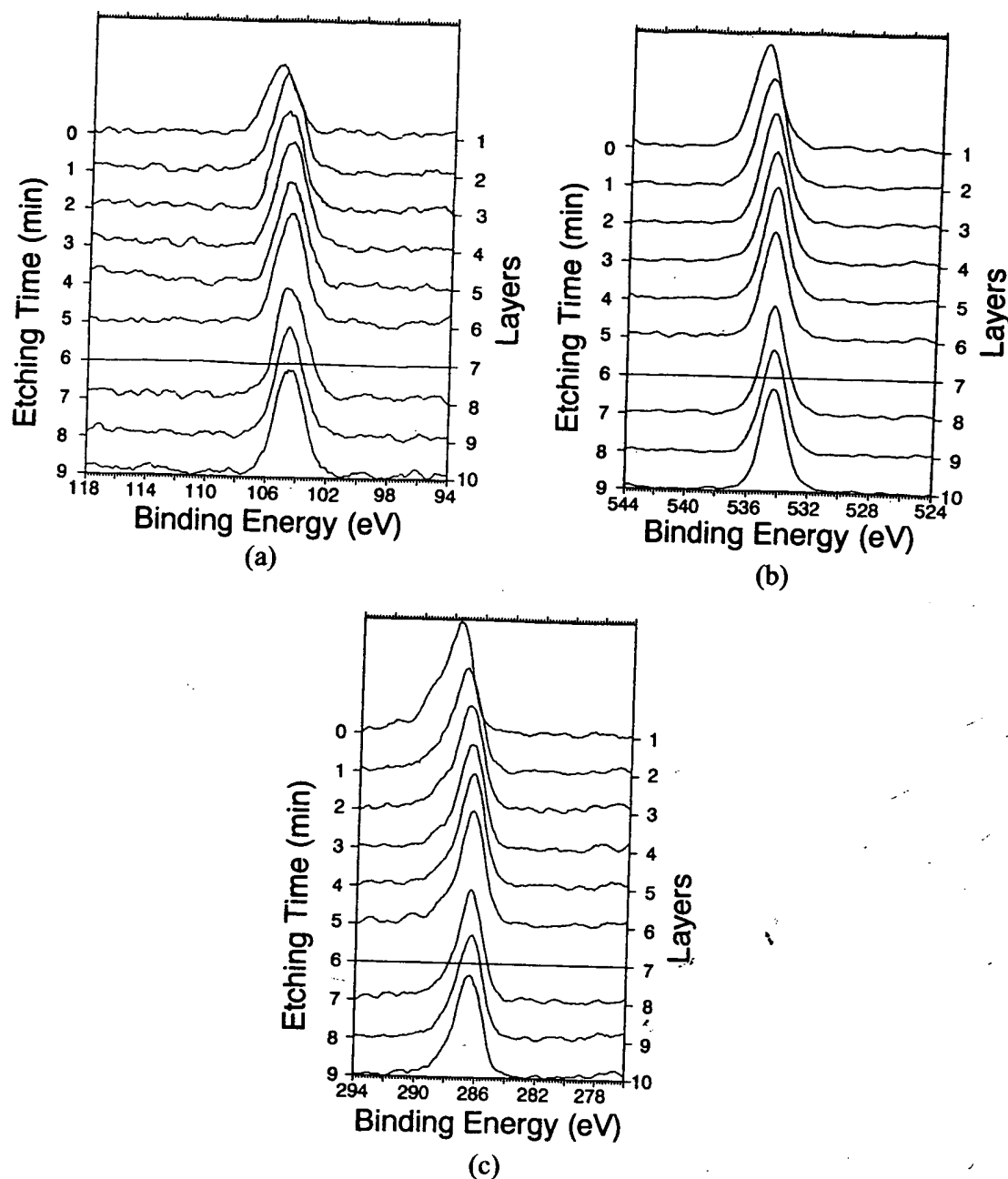
Figure 1. ESCA spectra of SiO_2-coated pure titanium surface at different depths after different argon-ion-etching times: (a) Si 2p, (b) O 1s, (c) C 1s.

positioned on the specimen with a micropipette. A tangent droplet was drawn from the point of air-water-metal intersection. Contact angles between this tangent line and the metal surface were measured under a microscope. For each type of metal substrate surface, five measurements were made and their mean was calculated.

RESULTS

Figure 1 shows the Si 2p spectra (a), O 1s spectra (b), and C 1s spectra (c) obtained at different depths of the SiO_2-coated

pure titanium casting surface after different argon-ion-etching times. The binding energies of the Si 2p and O 1s spectra for SiO_2 were 103.4 eV and 532.9 eV, respectively (JEOL, XPS Handbook, 1991). However, there were minute differences of approximately 1.3 eV between detected peak and binding energy. The thin SiO_2 film on the specimen surface might have caused the minute charge shift due to its insulation, because the same view was observed as in C 1s spectra [Fig. 1(c)]. Figure 2 shows the ESCA standard spectra obtained from SiO_2-coated pure titanium surface after 1 min of argon-ion-etching. As in the Si 2p spectra and O 1s spectra, the peak approximately corresponded to the binding energy of SiO_2,
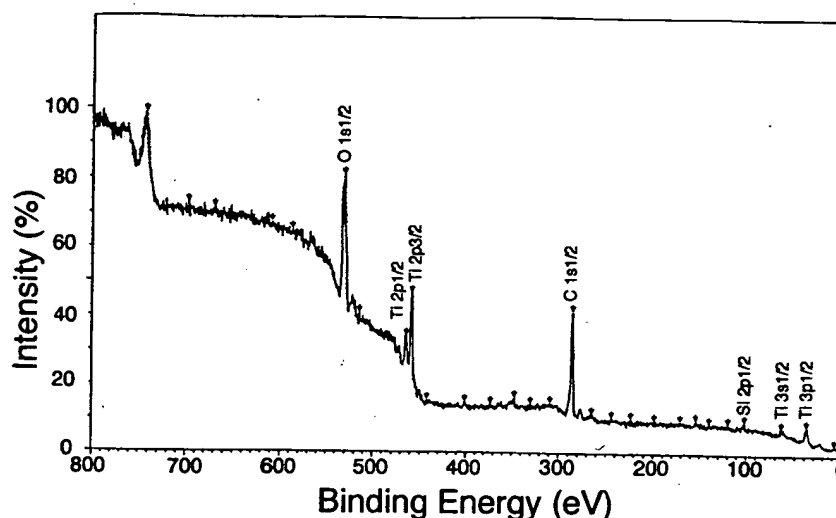
Figure 2. ESCA qualitative profile of SiO_2-coated pure titanium surface after 1 min of argon-ion-etching.

the SiO_2 film was confirmed to have formed on the pure titanium casting surface. Figure 3 shows the variations in concentration (at. %) of the elements in the SiO_2-coated pure titanium casting with depth. The composition ratio of O/Si is approximately 1.8, because the sintering temperature of 120 °C is not enough to remove all the C atoms from the SiO_2 film. The ESCA spectra (C 1s (a) and F 1s (b)) with argon ion etching for 9 min for SiO_2/F-coated pure titanium are shown in Figure 4. The binding energies of the C 1s and F 1s spectra for CF_2 were 292.2 eV and 689.7 eV, respectively. There were also minute differences of approximately 4.0 eV between detected peak and binding energy because of the minute charge shift. Thus, the peak approximately corresponded to the binding energy of CF_2.
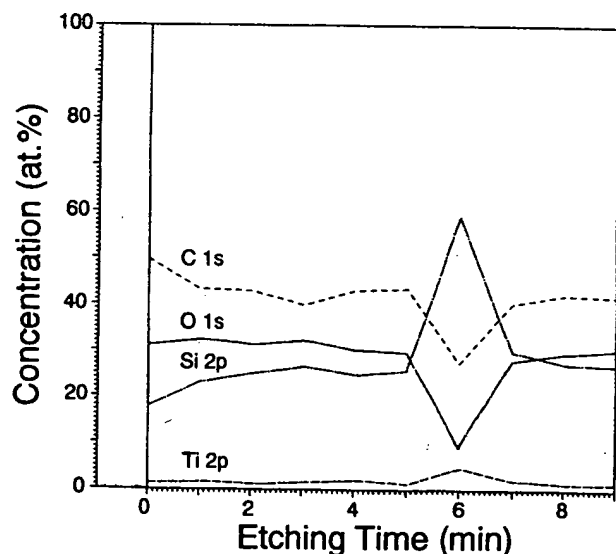

Figure 3. ESCA depth profile of SiO_2-coated pure titanium.

The adhesive bond strength between the SiO_2 or SiO_2/F-hybrid film and titanium metal substrate, amounts of titanium ions released from the specimens, and contact angles of water for three metal surface conditions are summarized in Tables I–III, respectively. The tensile bond strength of heated epoxy resin adhesive to alumina (stud-pin) was 77.3 ± 4.0 MPa, and the specimens failed at alumina-epoxy resin adhesive interface in the stud-pin. The tensile bond strength of SiO_2 or SiO_2/F-hybrid film to pure titanium showed above 55 MPa. However, all of the specimens coated with SiO_2 or SiO_2/F-hybrid film failed at the SiO_2 or SiO_2/F-hybrid film-epoxy resin adhesive interface, demonstrating that silica and fluorine peaks with the element of titanium as a substrate observed by the EDX analysis of the debonded SiO_2/F-coated metal surface (Fig. 5). Thus, the real bond strengths of both films to pure titanium casting are higher than the measured values. Both SiO_2- and SiO_2/F-coated specimens showed significantly less titanium ion release than noncoated specimens. For the SiO_2/F-coated titanium, the amounts of titanium ions release from the specimens were approximately 4% of those for noncoated metal. Both SiO_2- and SiO_2/F-coated surfaces showed an increase of contact angle of water, and their surfaces were more hydrophobic than the noncoated metal specimens.

DISCUSSION

There have been previous sol-gel studies in which liquid silicon alkoxides are transformed into a solid silicon-oxide network.[16-18] However, the feasibility of this method by dipping for the formation of a thin SiO_2 film on the surface of dental pure titanium casting has not been studied in detail.

As shown in Figure 6, the ESCA standard spectra obtained from SiO_2/F-hybrid-coated pure titanium surface after 1 min
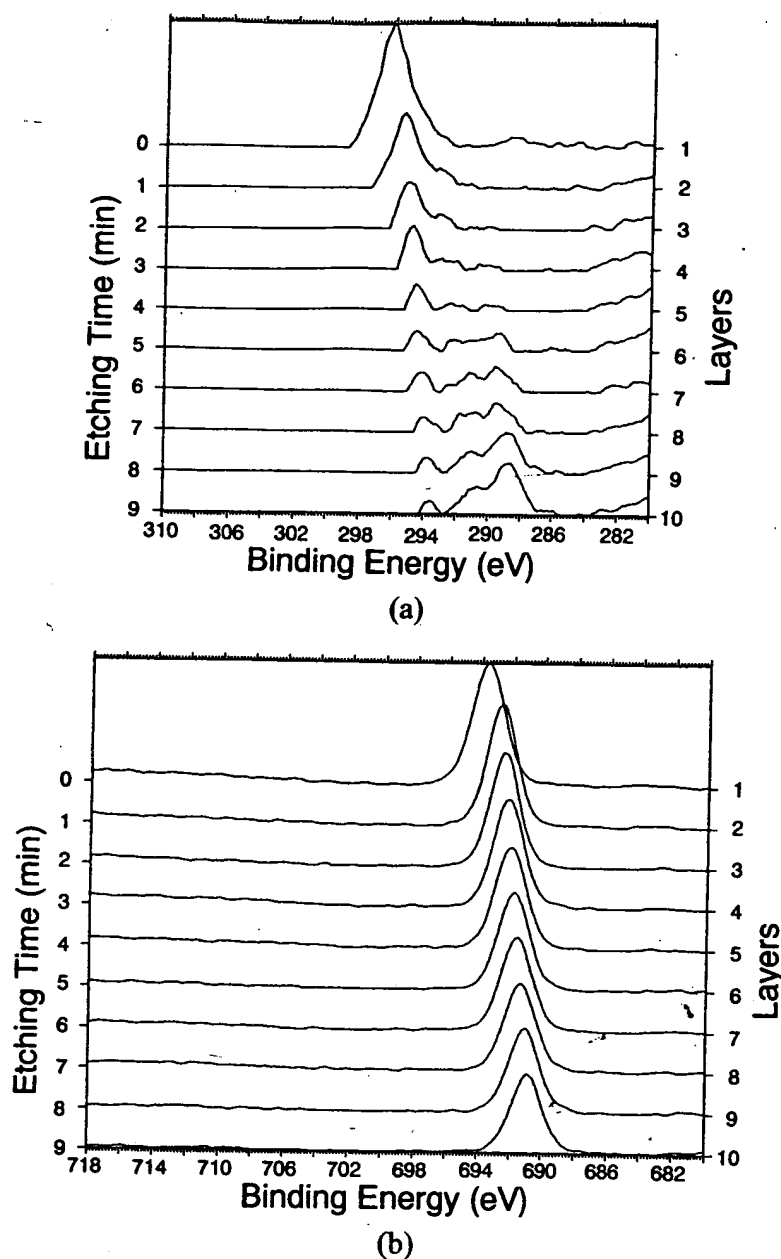
Figure 4. ESCA spectra of SiO_2/F-hybrid-coated pure titanium surface at different depths after different argon-ion-etching times: (a) C 1s, (b) F 1s.

of argon-ion-etching, SiO_2 films may react with carboxyl acid in fluoride polymer solution. Durable thin SiO_2 and SiO_2/F-hybrid films can be formed on the casting pure titanium surface. Titanium spontaneously forms a passivating oxide layer at room temperature when exposed to air or water. Thus, by the sol-gel dipping method, both SiO_2 and SiO_2/F-hybrid films could be formed onto the titanium oxide layer

TABLE I. Adhesive Bond Strength of SiO_2-Coated Film to Pure Titanium

Surface	Adhesive Strength ± SD (MPa)
Nontreatment	77.3 ± 4.0
SiO_2	55.7 ± 3.0
SiO_2/F	58.0 ± 2.7

TABLE II. Titanium Ion Release from Pure Titanium[a]

Surface	Titanium Ion ± SD (ppb/cm^2)
Nontreatment	235.2 ± 15.9[b]
SiO_2	30.5 ± 6.7[a]
SiO_2/F	9.5 ± 0.5[a]

[a] Values with different superscripts are significantly different ($p < 0.05$) by Duncan new multiple range test.

TABLE III. Contact Angle of Water[a]

Surface	Contact Angle $\pm$ SD (°)
Nontreatment	62.1 ± 2.8[a]
SiO_2	81.6 ± 3.3[b]
SiO_2/F	105.7 ± 1.3[c]

[a] Values with different superscripts are significantly different ($p < 0.05$) by Duncan new multiple range test.

generated on the pure titanium surface. By the sol-gel dipping method, a thin SiO_2 film could be formed onto the titanium oxide layer generated on pure titanium metal surfaces. It has been reported that, generally, oxidized metal on the metal surface bonded more strongly to SiO_2 than metal.[19] Although it was difficult to confirm Si–O–Ti bonds by ESCA analysis, the good adhesion in this study might come from Si–O–Ti bonds. The growth of a passivating oxide layer on the titanium surface increases at temperatures above 800 °C. However, the thicker the layer, the weaker the bonding.[20] Moreover, at this critical temperature, the thickness of the TiO_2-layer reaches a dimension that is undesirable.[21] The coating procedure of SiO_2 and SiO_2/F-hybrid films at 120 °C or 150 °C by sol-gel dipping method in our study has no negative influence on characteristics of the titanium oxide layer onto the substrate of pure titanium casting.

When dental metals are suspected to be an allergen source, all restorations must be replaced unless the metal containing the allergen is known. Patients are instructed to avoid exposure to materials containing allergens within their living environment. Of the base metals, titanium and its alloys may be one alternative replacement material for a patient who is sensitive to alloys and who needs prostheses. Titanium has never been reported to cause sensitivity reactions on oral mucosa because of the excellent corrosion resistance and low thermal conductivity of titanium. The corrosion resistance results from the strong tendency of titanium to form thermo-dynamically stable and mechanically adherent continuous

oxide layers on its surface.[22] However, there have been reports of patients suspected of exhibiting titanium allergy from implants.[23,24] The amounts of titanium ion released from SiO_2- and SiO_2/F-coated titanium were significantly less than those released from noncoated titanium. Thus, the formation of both thin SiO_2 and SiO_2/F-hybrid films by the sol-gel dipping process on the surface of restorations or prostheses made of pure titanium may minimize the possibility of hypersensitivity reactions to titanium ions.

Human periodontal disease occurs in response to the accumulation of dental plaque on tooth surfaces.[25–28] With either tooth enamel or a restorative material, gingival inflammation is caused by bacterial products elaborated within the dental plaque. The bacterial products are also the primary etiologic factor in dental caries.[29] The surfaces of dental restorations should, therefore, be as smooth as possible, minimizing plaque adherence.

The formation of bacterial plaque on tooth surfaces or various materials used in the fabrication of fixed prostheses such as metal or ceramic crown restorations has been studied extensively.[30–34] It has been reported that dental materials, regardless of their original surface properties, assume the same surface properties as the natural tooth surface and are covered with pellicle after only 1–2 h in the oral environment.[35] Low-energy surfaces were reported to collect less supragingival plaque than high-energy surfaces.[36] Glantz[37] concluded that the amount of plaque adhering to a solid surface under clinical conditions is positively correlated to the specific free energy of the solid. By comparing highly hydrophobic (low-energy) and hydrophilic (high-energy) surfaces, it is possible that there might be a critical level of surface hydrophobicity below which only very little accumulation of biofilm may occur.[38,39] The observations that the hydrophobic surface was highly resistant to both dental pellicle and plaque formation, and that even after 1 week in the oral environment it seemed to retain its original hydrophobic properties were unexpected. There was clearly more pellicle,
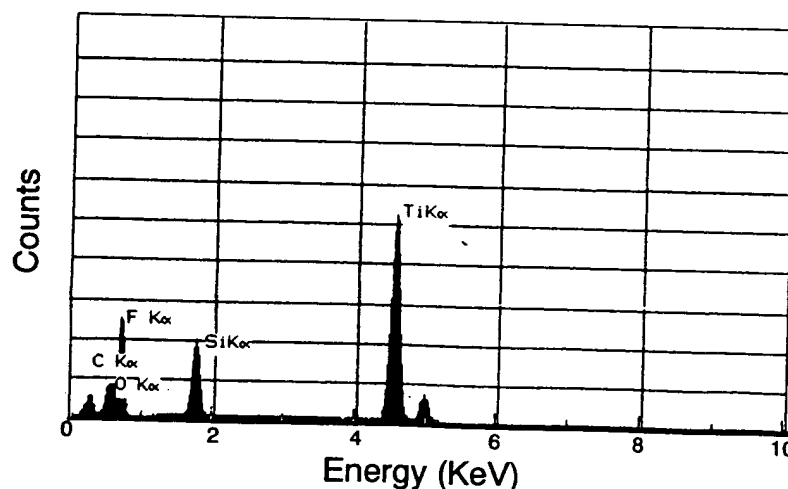

Figure 5. EDX analysis of debonded surface of SiO_2/F-hybrid-coated pure titanium.
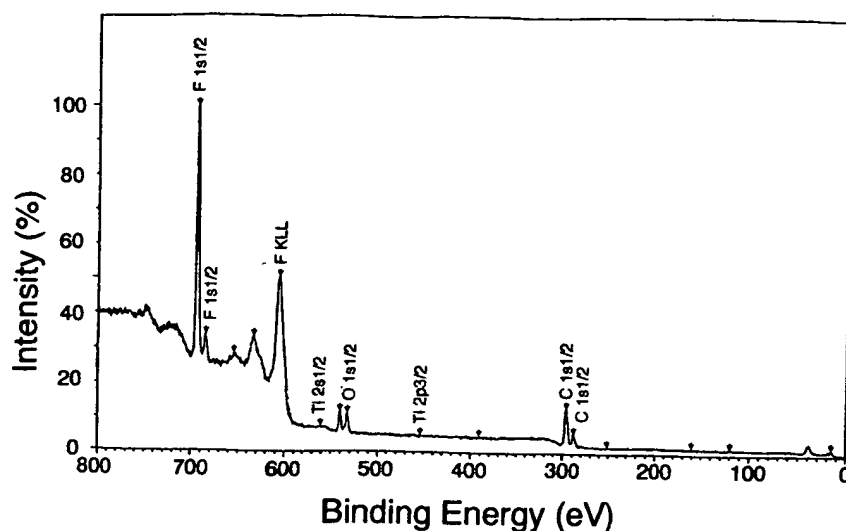
Figure 6. ESCA qualitative profile of SiO₂/F-hybrid-coated pure titanium surface after 1 min of argon-ion-etching.

and it adhered more strongly to the hydrophilic surface than to both hydrophobic and natural tooth surfaces.[38,39]

In the present study, more hydrophobic surfaces were obtained from the SiO_2- and SiO_2/F-coated pure titanium surfaces than noncoated metal surface. Thus, less plaque is expected to accumulate on the hydrophobic prosthesis surface on which both thin SiO_2 and SiO_2/F-hybrid films have been formed by the sol-gel dipping process. Furthermore, it may be virtually devoid of stainable pellicle. However, a more thorough clinical study is needed of dental plaque formation on the hydrophobic SiO_2- and SiO_2/F-coated surfaces, the durability of these films with long-term water immersion, and abrasion resistance to toothbrushing.

The shear bond strength between commercially available dental resin cements containing silica and pure titanium casting without any surface treatments was below 40 MPa.[40] In this study, thin SiO_2 and SiO_2/F-hybrid films coated by sol-gel dipping method could bond strongly to pure titanium casting surfaces (above 55 MPa of tensile strength). It appears that abrasion resistance of thin film coatings depends on the adhesive strength of films to metal substrate and on coating thickness. Therefore, we are performing another study of thicker SiO_2 film coatings in order to show the probability for good abrasion resistance to toothbrushing.

In conclusion, the formation of both thin SiO_2 and SiO_2/F-hybrid films by the sol-gel dipping process on the surface of dental pure titanium casting gave excellent surface properties including high bond strength to the metal substrate, extremely small amounts of titanium ions release, and high hydrophobicity. This may be useful clinically in enhancing the bond strength of dental resin cements to titanium, preventing titanium ions release from the substrate, and reducing the accumulation of dental plaque attaching to intraoral dental restorations.

We thank Dr. T. Inoi (Tokyo, Japan) for preparations and supplies of specimens.

REFERENCES

1. Albrektsson T, Zarb G, Worthington P, Eriksson AR. The long-term efficacy of currently used dental implants: a review and proposed criteria of success. Int J Oral Maxillofac Implants 1986;1:11–25.
2. Yamauchi M, Sakai M, Kawano J. Clinical application of pure titanium for cast plate dentures. Dent Mater J 1988;7:39–41.
3. Blackman R, Barghi N, Tran C. Dimensional changes in casting titanium removable partial denture frameworks. J Prosthet Dent 1991;65:309–315.
4. Lorey RE, Edge MJ, Lang BR, Lorey HS. The potential for bonding titanium restorations. J Prosthodont 1993;2:151–155.
5. Könönen M, Rintanen J, Waltimo A, Kempainen P. Titanium framework removable partial denture used for patients allergic to other metals: a clinical report and literature review. J Prosthet Dent 1995;73:4–7.
6. Castleman LS, Motzkin SM, Aricandri FP, Bonawit VL. Biocompatibility of nitinol alloys as an implant material. J Biomed Mater Res 1976;10:695–731.
7. Speek KM, Fraker AG. Anodic polarization behavior of It–N and Ti–6Al–4V in simulated physiological solutions. J Dent Res 1980;59:1590–1595.
8. Schröder H. Thin films. Phys 1969;5:87–141.
9. Sakka S. Treatise on materials science and technology. In: Tomozawa M, Doremus R, editors. Glass III. New York: Academic; 1982. p 129–167.
10. Klein LC. Sol-gel coatings in thin film processes, Vol II. Vossen JL, Kern W, editors. New York: Academic; 1991. p 501–522.
11. Brinker CJ, Hurd AJ, Frye GC, Schunk PR, Ashley CS. Sol-gel thin-film formation in chemical processing of advanced materials. Hench LL, West JK, editors. New York: Wiley; 1992. p 395–413.
12. Brinker CJ, Hurd AJ. Fundamental of sol-gel coating films. J Phys 1994;4:1231–1242.
13. Sakka S. Preparation and properties of sol-gel coating films. J Sol-Gel Sci Tech 1994;2:451–455.
14. Yoshida K, Funaki K, Tanagawa M, Matsumura H, Tanaka T, Atsuta M. Properties of commercially available luting cements. J Jpn Prosthodont Soc 1995;39:35–40.
15. Tiller HJ, Göbel R, Magnus B, Musil R, Bimberg R. Werkstoffliche Grundlagen zum Silicoater-MD-Verfahren. Dent Labor 1990;38:78–82.

16. Komiya K, Sakka S. TiO$_2$-SiO$_2$ glasses from metal alkoxides. J Mater Sci Lett 1980;15:2937-2939.

17. Gonzalez-Oliver CJR, James PF, Rawson H. Silica and silica-titania glasses prepared by the sol-gel process. J Noncryst Solids 1982;48:129-152.

18. Dislich H. Glassy and crystalline systems from gels: chemical basis and technical application. J Noncryst Solids 1983;57:371-388.

19. Iwata S, Hara N, Kobayashi N. Evaluation of adherence of chemical-vapor-deposited tungsten to SiO$_2$. J Jpn Inst Metals 1989;53:114-118.

20. Hautaniemi JA, Herø H, Juhanoja JT. On the bonding of porcelain on titanium. J Mater Sci Mat Med 1992;3:186-191.

21. Nordström EG, Södergård BE, Kukkonen L. Thin sol-gel-derived silica-coatings on CP-titania and bioactivity thereupon. Biomed Mater Eng 1994;4:187-192.

22. Schutz RW, Thomas DE. Corrosion of titanium and titanium alloys. In: ASM Handbook Committee. Metals handbook. 9th Ed. Metals Park, Ohio: ASM Int; 1987. p 669-706.

23. Mitchell DL, Synnott SA, VanDercreek JA. Tissue reaction involving an intraoral skin graft and CP titanium abutments: a clinical report. Int J Oral Maxillofac Implants 1990;5:79-84.

24. Lalor PA, Revell PA, Gray AB, Wright S, Railton GT, Freeman MAR. Sensitivity to titanium. A cause of implant failure? J Bone Joint Surg 1991;73-B:25-28.

25. James PMG, Jackson D, Slack GL, Lawton FE. Gingival health and dental cleanliness in English school children. Arch Oral Biol 1960;3:57-60.

26. O'Leary TL, Shannon IL, Prigmore JR. Clinical correlations and systemic status in periodontal disease. J Periodontol 1962; 33:243-250.

27. Loe H, Theilade E, Jensen SB. Experimental gingivitis in man. J Periodontol 1965;36:177-180.

28. Dale JW. Toothbrushing frequency and its relationship to dental caries and periodontal disease. Aust Dent J 1969;14:120-123.

29. Dummer RM, Harrison KA. In vitro plaque formation on commonly used dental materials. J Oral Rehabil 1982;9:413-417.

30. Chan C, Weber H. Plaque retention on teeth restored with full-ceramic crowns: a comparative study. J Prosthet Dent 1986; 56:666-671.

31. Shafagh I. Plaque accumulation on cast gold complete crowns polished by a conventional and an experimental method. J Prosthet Dent 1986;55:339-342.

32. Savitt ED, Malament KA, Socransky SS, Molcer AJ, Backman KJ. Effects on colonization of oral microbiota by a cast glass-ceramic restoration. Int J Periodont Restora Dent 1987;2:22-35.

33. Adamczyk E, Spiechowicz E. Plaque accumulation on crowns made of various materials. Int J Prosthodont 1990;3:285-291.

34. Wallman C, Krasse B. Mutans streptococci in margins of fillings and crowns. J Dent 1992;20:163-166.

35. Jendresen MD, Glantz PO. Clinical adhesiveness of selected dental materials: an in-vivo study. Acta Odontol Scand 1981; 39:39-45.

36. Quirynen M, Marechal M, Busscher HJ, Weerkamp AH, Arends J, Darius PL, Steenberghe D. The influence of surface free-energy on planimetric plaque growth in man. J Dent Res 1989; 68:796-799.

37. Glantz PO. The adhesiveness of teeth. J Colloid Interface Sci 1971;37:281-290.

38. Olsson J, Carlén A, Holmberg K. Inhibition of Streptococcus mutans adherence by means of alkyl phosphates and nonionic surfactants. Caries Res 1991;25:51-57.

39. Olsson J, Van der Heijde Y, Holmberg K. Plaque formation in vivo and bacterial attachment in vitro on permanently hydrophobic and hydrophilic surfaces. Caries Res 1992;26: 428-433.

40. Taira Y, Yoshida K, Matsumura H, Atsuta M. Phosphate and thiophosphate primers for bonding prosthodontic luting materials to titanium. J Prosthet Dent 1998;79:384-388.

JOURNAL OF MEDICAL MATERIALS RESEARCH

APPLIED BIOMATERIALS